Single-Crystal Studies of Osmium Dihydrogen Dihydride Complexes

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Single-crystal neutron diffraction has played the major role in our understanding of the structure and bonding of hydrogen to transition metals in coordination complexes. Many types of hydride complexes in mononuclear and cluster compounds have been characterized in recent years, as well as molecules containing carbon-hydrogen-metal three-center (agostic) interactions and molecular dihydrogen complexes. Following the discovery of the first stable molecular dihydrogen complex by Greg Kubas of Los Alamos National Laboratory in the early 1980s (Kubas, 1988), about 10 single-crystal neutron structures have been reported. The majority of these structures are based on data obtained by Tom Koetzle, Alberto Albinati, and co-workers at the Brookhaven High Flux Beam Reactor (Koetzle, 1995). Inelastic neutron scattering has also played an important role in investigations of the dynamical rotation of the bound dihydrogen ligands (Eckert and Kubas, 1993). At the IPNS, using data obtained with the single-crystal diffractometer, we have recently

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characterized a series of three osmium-dihydrogen-dihydride complexes. This series provides systematic "snapshots" of points along the reaction pathway of the oxidation addition of dihydrogen to a transition metal to form a dihydride complex (Fig. 1).

As shown schematically in Fig. 1, the sideways addition of dihydrogen can initially produce a three-center moiety. Activation of the H_2 bond results in cleavage of the H_2 molecule and formation of the dihydride.
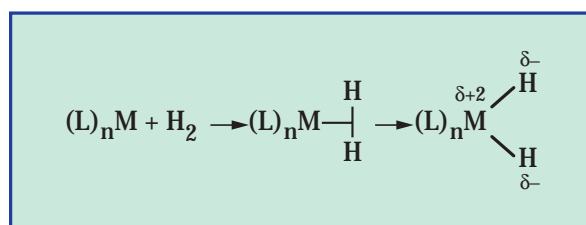

Figure 1
Oxidative addition of molecular dihydrogen at a transition metal center (M) to form a dihydride complex, where $(L)_n$ indicates n *other ligands L.*

As shown in Fig. 2, activation or weakening of the H_2 bond can occur through a dative bond donation of the H_2 σ-bonding electrons to the metal, or back-donation from a metal π-orbital to the σ^*-antibonding H_2 orbital, or both.

Compounds with the general formula $[(C_5Me_5)Os(\eta^2\text{-}H_2)(H)_2(L)][BF_4]$ (Me = CH_3), where L is a phosphine or arsine ligand, were prepared by protonation of the neutral trihydride complex $(C_5Me_5)OsH_3(L)$. Shown in Fig. 3(a) is the single-crystal neutron structure of the cationic complex at 20 K with L = PPh_3 (Ph = C_6H_5), compound **1** (Gross *et al.*, 1997). The cation has a four-legged "piano stool" geometry, with the phosphine and two classical hydride
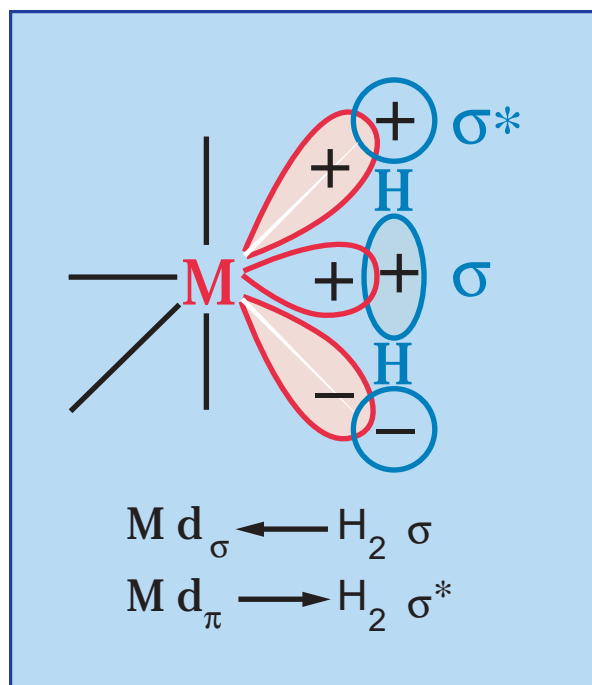
Figure 2
Bonding between a transition metal and a
dihydrogen ligand showing σ_{H-H} *bonding orbital*
to the metal and π*-backbonding from the metal*
to the antibonding σ^*_{H-H} *orbital.*

ligands making up three of the legs. Located *trans* to the phosphine and *cis* to the two classical hydrides is a dihydrogen ligand with an elongated H–H distance of 1.01(1) Å. In free hydrogen, the H–H distance is 0.74 Å, and distances of less than 1.0 Å are typical of "normal" dihydrogen complexes. Distances of about 1.0 to 1.4 Å are considered elongated or partially activated, and H–H distances greater than 1.5 Å for hydrogens bound to a metal center are considered classical hydrides. The H–H vector in compound **1** is nearly parallel to the Os–Cn (Cn = C_5Me_5 centroid) vector.

In a second structural analysis, shown in Fig. 3(b), triphenylphosphine, PPh_3, is replaced by triphenylarsine, $AsPh_3$,

compound **2**, to yield a similar structure but with an H–H distance of 1.08(1) Å. The increase in the H–H distance may indicate greater π-bond donation from As into the Os *d* orbital, which also π-backbonds to the H_2 σ^* orbital. The crystal structures of compounds **1** and **2** are essentially isomorphous, with identical monoclinic space groups.

Finally, the structure of the complex with triscyclohexylphosphine, $P(c\text{-Hx})_3$, (c-Hx = C_6H_{11}) as the ligand, compound **3**, was examined. In this case, the crystal is triclinic, and the molecular structure is shown in Fig. 3(c). The dihydrogen appears to have rotated 90°, such that all four hydrogen ligands are now coplanar with each other. In addition, the dihydrogen H–H distance has increased to 1.31(1) Å. Another intriguing feature of the structure of compound **3** is that the C_5Me_5 ligand is rotated by about 20° relative to its orientation in **1** and **2**, indicating a change in the electronic structure of the osmium metal center.

When the H–H axis is parallel with the M–Cn axis, as in **1** and **2**, the dihydrogen ligand is stabilized by π-backbonding from the metal center. When the H–H axis is perpendicular to the M–Cn axis, as in **3**, there can be a "*cis*" interaction with the classical hydride ligands that could stabilize the H_2 ligand. In such a configuration, the osmium-hydride bonds donate electron density into the H–H σ^* orbital, which weakens the H–H bond and thereby creates nascent bonds between the classical hydride ligands and the molecular H_2 ligand. In the PPh_3 and $AsPh_3$ compounds (**1** and **2**), the π-backbonding is the dominant effect, and the H_2 ligand is oriented parallel with the Os–Cn axis.

In the $P(c\text{-Hx})_3$ compound, **3**, by contrast, the interactions with the *cis* Os–H bonds are
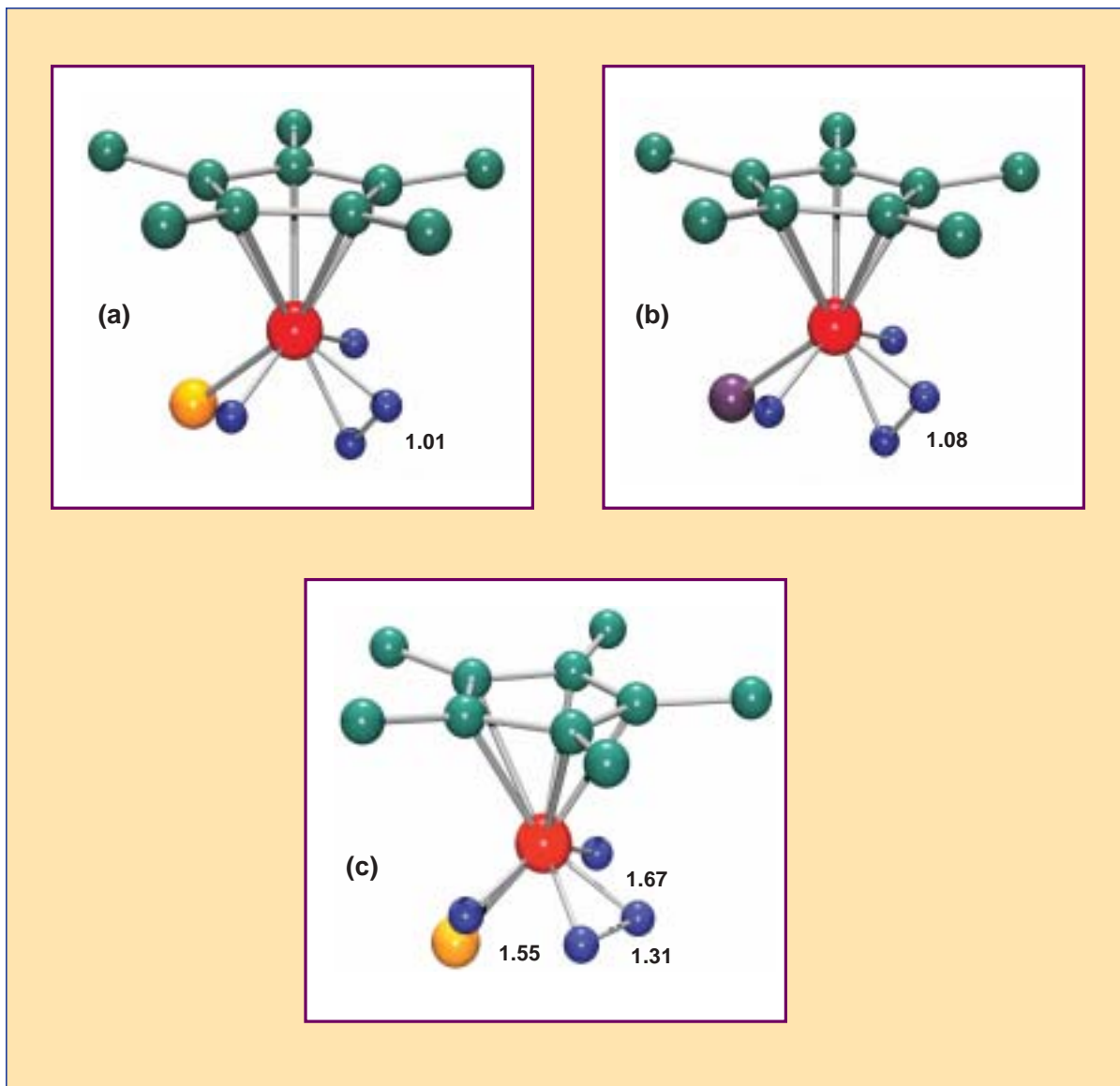
Figure 3

The structures of (a) Compound *1*: [(C₅Me₅)Os(η²-H₂)(H)₂(PPh₃)]⁺, (b) Compound *2*: [(C₅Me₅)Os(η²-H₂)(H)₂(AsPh₃)]⁺, and (c) Compound *3*: [(C₅Me₅)Os(η²-H₂)(H)₂(P(c-Hx)₃)]⁺. The view of the molecule relative to the P–Os–Cn plane is the same in each case. For clarity, the drawings do not show the phenyl and cyclohexyl groups bound to phosphorus or arsenic and the methyl hydrogen atoms on the C₅Me₅ ligand.

dominant. This is a surprising result; $P(c\text{-}Hx)_3$ is by far the strongest σ-donor of the three Lewis bases investigated, and thus we expected that π-backbonding from the metal should be strongest in this compound. A possible explanation is that the stronger donor $P(c\text{-}Hx)_3$ makes the classical hydride ligands more hydridic, thus strengthening the *cis* interactions that stabilize the rotamer in which the H–H bond is perpendicular to the Os–Cn axis.

As mentioned above, compounds **1** through **3** appear to depict the reaction pathway of the oxidative addition of dihydrogen to a transition metal. In addition, compound **3** is a possible midway point in the exchange of the classical and nonclassical hydrogen atom sites. This exchange is observed in the ^{1}H NMR of these complexes down to approximately –100°C or lower (Gross *et al.*,

1997). A similar intramolecular hydrogen exchange is observed in a series of iridium dihydrogen dihydride complexes, $IrX(H)_2(\eta^2\text{-}H_2)(PR_3)_2$ for X = Cl,Br,I and R = H,Me (Li *et al.*, 2000). In these iridium systems, calculations indicate that the mechanism of the exchange process involves rotation and oxidative addition of the dihydrogen to form an intermediate tetrahydride complex. Another possible mechanism for intramolecular exchange is described as an attractive *cis*-effect between dihydrogen and hydride ligand atoms in the complex $Fe(H)_2(\eta^2\text{-}H_2)(PEtPh_2)_3$ $(Et = C_2H_5)$ (Van Der Sluys *et al.*, 1990) similar to that described above for **3**. In this mechanism, a tetrahydride intermediate is not encountered. Calculations are currently underway to provide insight into the structure and bonding in the series of osmium complexes that were characterized with the IPNS SCD.

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